(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number
WO 01/02624 A1

(51) International Patent Classification[7]: C25B 1/00

(21) International Application Number: PCT/EP00/06350

(22) International Filing Date: 4 July 2000 (04.07.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99810592.8 5 July 1999 (05.07.1999) EP

(71) Applicant *(for all designated States except US)*: **ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)** [CH/CH]; SRI, CH-1015 Lausanne (CH).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **GRÄTZEL, Michel** [DE/CH]; Chemin du Marquisat 7a, CH-1025 St. Sulpice (CH). **AUGUSTYNSKI, Jan** [CH/CH]; Rue Louis-Curval 1, CH-1206 Genève (CH).

(74) Agent: **HAMMER, Bruno**; Sunneraiweg 21, CH-8610 Uster (CH).

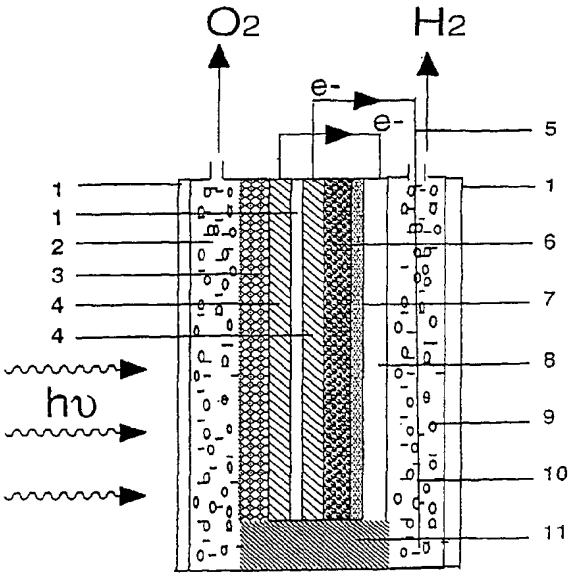
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT



(57) Abstract: The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

WO 01/02624 A1

TANDEM CELL FOR WATER CLEAVAGE BY VISIBLE LIGHT

The invention is related to a photoelectrochemical system for the cleavage of water to hydrogen and oxygen according to the preamble of the independent claim 1.

Previous systems that accomplish the direct splitting of water by visible light with a comparably high efficiency employ very expensive single crystal semiconductor materials. For details see O.Khaselev and J.Turner, Science 280, 1998, 455). Therefore these previous systems are not suitable for practical applications to produce hydrogen and oxygen from sunlight.

According to the invention a photoelectrochemical system is characterized by the features of the characterizing part of the independent claim 1. The depending claims are related to particularly favorable embodiments of the invention. The improved photoelectrochemical system provides for photoelectrochemical tandem cells that show a considerably high efficiency. Further the photoelectrochemical system can be manufactured at relatively low cost. A further advantage of the present invention is that seawater can be used for the process instead of pure water.

Description of the invention, device structure.

In the following the invention will now be described by way of example and with reference to the accompanying drawings that show the following:

Fig. 1 shows a schematic drawing of the water photolysis device that is the object of the present invention.

Fig. 2 shows the spectral dependency of the photon-to electric current conversion achieved with the sensitized TiO_2 films for several ruthenium complexes; it shows the incident photon to current conversion efficiencies obtained with various sensitizer;

Fig. 3 shows an energy level diagram that illustrates the functioning of the tandem cell; it shows the Z scheme of biphotonic water photolysis

A schematic representation of the water photolysis device, that is the object of the present invention is described is illustrated in Fig. 1. The device consists of two photo systems connected in series. The cell on the left contains the aqueous electrolyte that is subjected to water photolysis. The electrolyte is composed of water as a solvent to which an electrolyte has been added for ionic conduction. Saline seawater can also be used as a water source in which case the addition of electrolyte becomes superfluous. Light enters from the left side of the cell through a glass window (1). After traversing the electrolyte (2) it impinges on the back wall of the cell constituted by a mesoporous semiconductor film composed of an oxide such as WO_3 or Fe_2O_3 (3), The latter is deposited onto a transparent conducting oxide film (4), made from a material such as fluorine doped tin dioxide that serves as current collector which is deposited on the glass sheet (1). The oxide absorbs the blue and green part of the solar spectrum while the yellow and red light is transmitted through it. The yellow and red part of the solar spectrum is captured by a second cell mounted behind the back wall of the first cell. The second cell contains a dye sensitized mesoporous TiO_2 film. Its functions as a

light driven electric bias increasing the electrochemical potential of the electrons that emerge from the WO_3 film under illumination to render the reduction of water to hydrogen possible. It consists of a transparent conducting oxide film (4) deposited on the back side of the glass sheet (1) constituting the back wall of the first cell. The conducting oxide film is covered by the dye-derivatized nanocrystalline titania film (6). The latter is in contact with the organic redox electrolyte (7) and the counter electrode (8) consisting of a glass which is rendered conductive on the side of the organic electrolyte by deposition of a transparent conductive oxide layer. Behind the counterelectrode there is a second compartment (9) containing an aqueous electrolyte of the same composition as in the front compartment (2). Hydrogen is evolved at the cathode (10) which is immersed in this second electrolyte compartment. The two electrolyte compartments (2) and (10) have the same composition and are separated by an ion conducting membrane or a glass frit (11).

We shall now discuss a specific embodiment of such a tandem device achieving the direct cleavage of water into hydrogen and oxygen by visible light. A thin film of nanocrystalline tungsten trioxide absorbs the blue part of the solar spectrum.

$$WO_3 + h\nu \quad \Rightarrow \quad WO_3 (e^-, h^+)$$

The valence band holes (h^+) created by band gap excitation of the oxide serve to oxidize water forming oxygen and protons:

$$4h^+ + H_2O \quad \Rightarrow \quad O_2 + 4H^+$$

while the conduction band electrons are collected on the conducting glass support forming the back wall of the first photocell. From there on they are fed into the second photocell that consists of a dye sensitized nanocrystalline TiO_2 film. The latter is mounted directly behind the WO_3 film capturing the green and red part of the solar spectrum that is transmitted through the top electrode. The role of the second photocell is merely that of a photo driven bias. The electrochemical potential of the electrons is

sufficiently increased by passing through the second photocell that they can reduce the protons produced during water oxidation to hydrogen.

$$4\,H^+ + 4\,e^- \Rightarrow 2\,H_2$$

The overall reaction corresponds to the splitting of water by visible light.

$$H_2O \Rightarrow H_2 + 0.5\,O_2$$

Semiconducting oxides, such as WO_3 and Fe_2O_3 are the materials of choice for the photo-anode as they are stable under operation resisting to both dark and photo corrosion. Tungsten trioxide and ferric oxide are so far the only known and readily available oxide semiconductors that are capable of producing oxygen using visible light. The electrons generated in the oxide are collected by the conducting glass and are subsequently fed into a second photocell that is placed directly behind the oxide film. The photo-active element of this second cell is a dye sensitized mesoporous TiO_2 capturing the yellow and red light that is transmitted through the oxide electrode. It serves as a photo- driven bias increasing the electrochemical potential of the photoelectrons produced by band gap excitation of the oxide to render reduction of water to hydrogen feasible.

Fig. 2 presents the spectral dependency of the photon-to electric current conversion achieved with the sensitized TiO_2 films for several ruthenium complexes. Very high efficiencies of current generation, exceeding 75% are obtained. When corrected for the inevitable reflection and absorption losses in the conducting glass that serves to support the film the yields are practically 100 percent. For the dyes $RuL_2(SCN)_2$ and $RuL'(SCN)_3$ the photo-response of the film extends well into the red and near infrared part of the spectrum making these complexes an appropriate choice for the harvesting of the red and yellow part of sun light by the second photocell in the tandem system .

The functioning of the tandem cell is further illustrated by the energy level diagram shown in Fig. 3. There is close analogy to the Z-scheme operative in the light reaction in green plants in which the two photo systems are connected in series, one affording

oxidation of water to oxygen and the other generating the NADPH used in CO_2 fixation. At this stage of development the overall AM 1.5 solar light to chemical conversion efficiency achieved stands at 5 %.

Working Example

The preparation of transparent mesoporous WO_3 films of a few micron thickness has been achieved via a sol-gel type process. A colloidal WO_3 precursor solution was prepared first and after mixing with polyvinyl alcohol, films were deposited on conducting glass (Nippon Sheet Glass, 10 ohm/o, fluorine-doped SnO_2 glass (TCO)) surface. In order to supply the bias necessary to reach the plateau photocurrent, two in series connected sensitized mesoporous TiO_2 injection cells were placed under the transparent WO_3 film. This configuration reached a photocurrent of 3.5 mA/cm^2 for hydrogen generation in simulated AM 1.5 sunlight. This corresponds to an overall solar to chemical conversion efficiency of 5 % for light induced water cleavage by AM 1.5 standard sunlight.

This example illustrates the successful operation of the tandem device which is the object of the present invention. It is based on two superimposed photocells having complementary light absorption in the visible and near infrared range according to the embodiment described in the patent disclosure. Such a tandem cell accomplishes the splitting of water into hydrogen and oxygen by visible light directly rendering the use of a separate electrolysis cell superfluous. Thus it is preferred over alternative systems where traditional photovoltaic cells, such as silicon solar cells are used in conjunction with a water electrolyzer. The present invention renders the water electrolyzer superfluous reducing the cost of the water splitting device substantially. Apart from the cost there it is also advantageous from the operational point of view. In the conventional photoelectrolysis systems based on the combination of silicon solar cells with a water electrolyzer, several photovoltaic cells have to be connected in series to yield the voltage of about 1.7 V required for the operation of the water electrolyzer. Furthermore each of the photovoltaic cells should operate at its optimum power point

to keep losses low and the efficiency high. However as the power point fluctuates according to the intensity and spectral distribution of the incident solar radiation one needs to install a very complicated system that changes the number of in series connected cells in response to the meteorological conditions. This renders the system expensive and it operation complex. In contrast the tandem cell described by the present invention operates at practically the same efficiency irrespective of the intensity and spectral distribution of the incident solar light.

The additional advantage of the present invention is that it uses low cost materials, the semiconductor layers employed being made from cheap and readily available oxide films having a mesoporous morphology. The tandem cell exhibits an overall conversion efficiency of 5 % for the photo cleavage of water into hydrogen and oxygen.

A further advantage of the present invention is that seawater can be employed instead of pure water. The salt contained in seawater produces the ionic conductivity required for operating the water cleavage device. This safes the cost for desalination of the water and for providing the electrolyte supplement which is required if pure water is employed in the electrolyzer.

The invention relates to a tandem device based on two superimposed photocells having complementary light absorption in the visible and near infrared range. Such a tandem cell accomplishes the splitting of water into hydrogen and oxygen by visible light directly rendering the use of a separate electrolysis cell superfluous. The additional advantage of the present invention is that it uses low cost materials, the semiconductor layers employed being made from cheap and readily available oxide films having a mesoporous morphology. The tandem cell exhibits an overall conversion efficiency of 5 % for the photo cleavage of water into hydrogen and oxygen.

The tandem cell or photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically. The photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution. This semiconducting oxide absorbs

the blue and green part of the solar emission spectrum of a light source or light sources and generates with the energy collected oxygen and protons from water. The not absorbed yellow and red light transmits the top cell and enters a second photocell, the bottom cell, which is mounted, in the direction of the light behind, preferably directly behind the top cell. The bottom cell includes a dye sensitized mesoporous photovoltaic film. The bottom cell converts the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons which are produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

Although the use of the photoelectrochemical system with the tandem cell according to the invention can be most advantageously used with sun light, it can be driven with the light of any light source or light sources that emit light of the required frequencies.

The reference numbers used in Fig. 1 denominate the following:

1 Glass sheet

2 Aqueous electrolyte

3 Mesoporous oxide film, e.g., WO_3 Fe_2O_3

4 Transparent conducting oxide (TCO) film

5 Electrical connection

6 Dye sensitized mesoporous Tio2 film

7 Organic redox electrolyte for dye sensitized solar cell (DYSC), used in tandem

8 Counter electrode for DYSC

9 Aqueous electrolyte (same composition as 2)

10 Catalytic cathode for H_2 evolution

11 Glass frit

Claims

1. A photoelectrochemical system for the cleavage of water to hydrogen and oxygen by visible light consisting of two superimposed photocells, both cells being connected electrically, characterized in that the photoactive material in the top cell is a semiconducting oxide placed in contact with an aqueous solution, said oxide absorbing the blue and green part of the solar emission spectrum to generate oxygen and protons from water and transmitting the yellow and red light to a second photocell mounted behind the top cell and composed of a dye sensitized mesoporous photovoltaic film, said bottom cell converting the yellow, red and near infrared portion of the sunlight to drive the reduction of the protons, produced in the top cell during the photo catalytic water oxidation process, to hydrogen.

2. A photoelectrochemical system for the direct cleavage of water to hydrogen and oxygen by visible light according to claim 1, consisting of two superimposed photocells, both cells being connected electrically, wherein the photoactive material present in the top photocell is a thin film of WO_3 or Fe_2O_3 deposited on a conducting substrate or conducting glass and placed in contact with an aqueous electrolyte solution, said WO_3 tungsten oxide or Fe_2O_3 iron oxide absorbing the blue and green part of the solar emission spectrum to generate oxygen and protons from water and transmitting the yellow and red light to a bottom photocell mounted behind the top photocell and composed of a dye sensitized photovoltaic film, said second photocell converting the yellow, red and near infrared portion of the solar emission spectrum to drive the reduction of the protons, produced in the top photocell during the water oxidation process, said reduction of protons to hydrogen gas taking place in an electrolyte compartment mounted behind the bottom photocell and being separated from the top photocell compartment where oxygen is evolved by a glass frit or an ion conducting membrane.

3. A photoelectrochemical system according to claim 1 or 2, characterized in that the photoactive oxide material present in the top cell is a doped form of Fe_2O_3, the dopant being selected from the elements Si, Ge, Sn, Pb, Ti, Zr. Hf, Sb, Bi, V, Nb, Ta, Mo, Tc, and Re or F, Cl, Br and I.

4. A photoelectrochemical system according to claim any of claims 1 to 3, characterized in that the photoactive Fe_2O_3 in the doped or undoped form is present as a smooth layer, said layer having a thickness between 50 nm and 5000 nm said layer transmitting light of wavelength above 600 nm.

5. A photoelectrochemical system according to any of claims 1- 4, characterized in that the sensitizer is a ruthenium polypyridyl complex chosen from $RuL_2(NCS)_2$ and RuL'$(NCS)_3$, where L = 4,4'-dicarboxy-2,2'-bipyridine and L' = 4,4'4''-tricarboxy-2,2',6',2''-terpyridine.

6. A photoelectrochemical system according to any of claims 1-5, characterized in that the oxygen and hydrogen evolution reaction take place both in the top cell and/or in separated compartments, said compartments being connected by an ion conducting membrane or a glass frit.

7. A photoelectrochemical system according to any of claims 1 –6, characterized in that the hydrogen evolution is catalyzed by a metal, chosen from Ni, Pt, Pd, Ru, Rh and Ir ,or alternatively by a polyacid or heteropolyacid chosen from tungsten, vanadium and molybdenum., said catalyst being deposited in the form of a thin coating on the cathode of the cell.

8. A photoelectrochemical system according to any of claims 1-7, characterized in that seawater is used as a source for hydrogen and oxygen in the water cleavage or water splitting device.

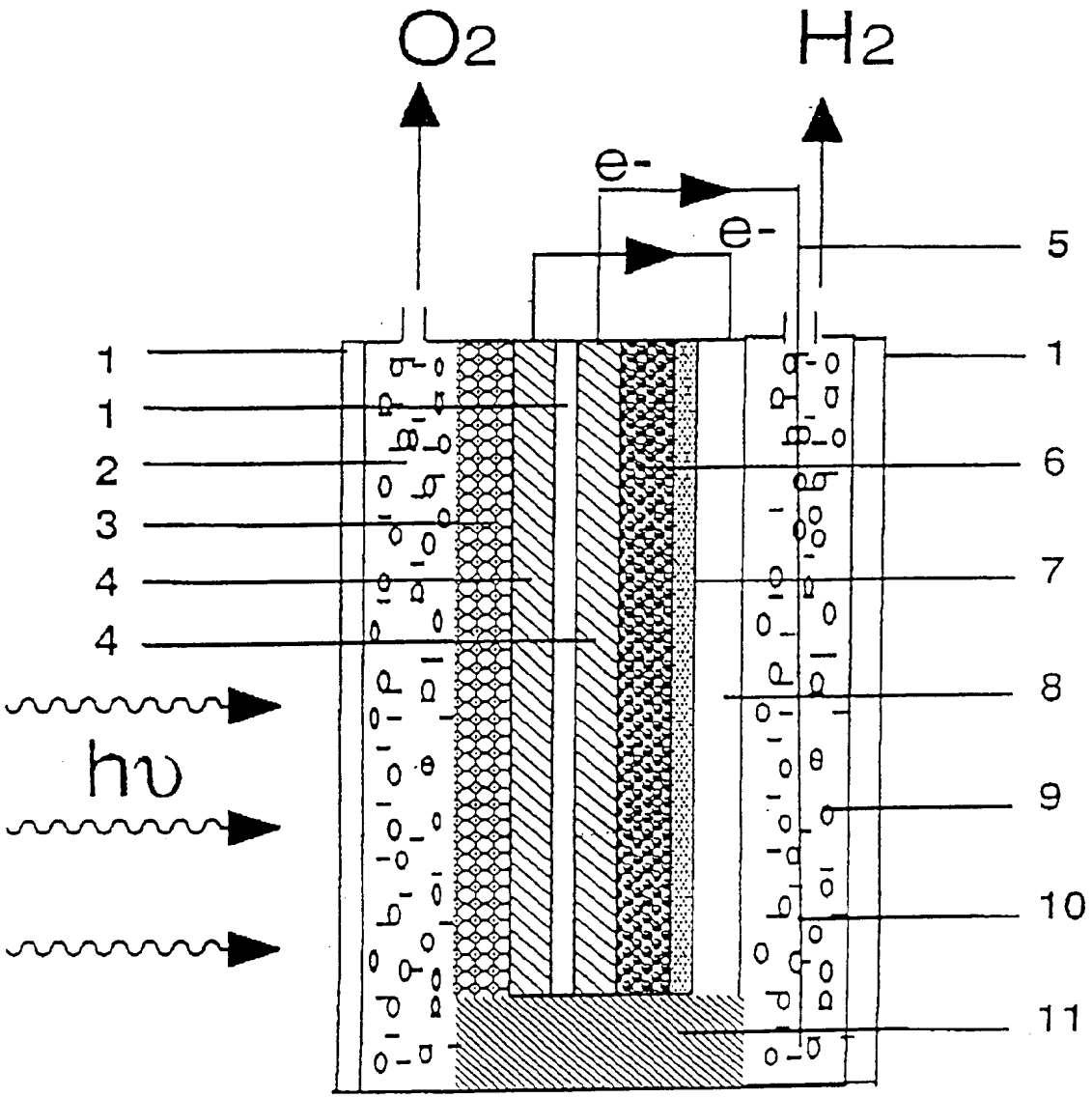
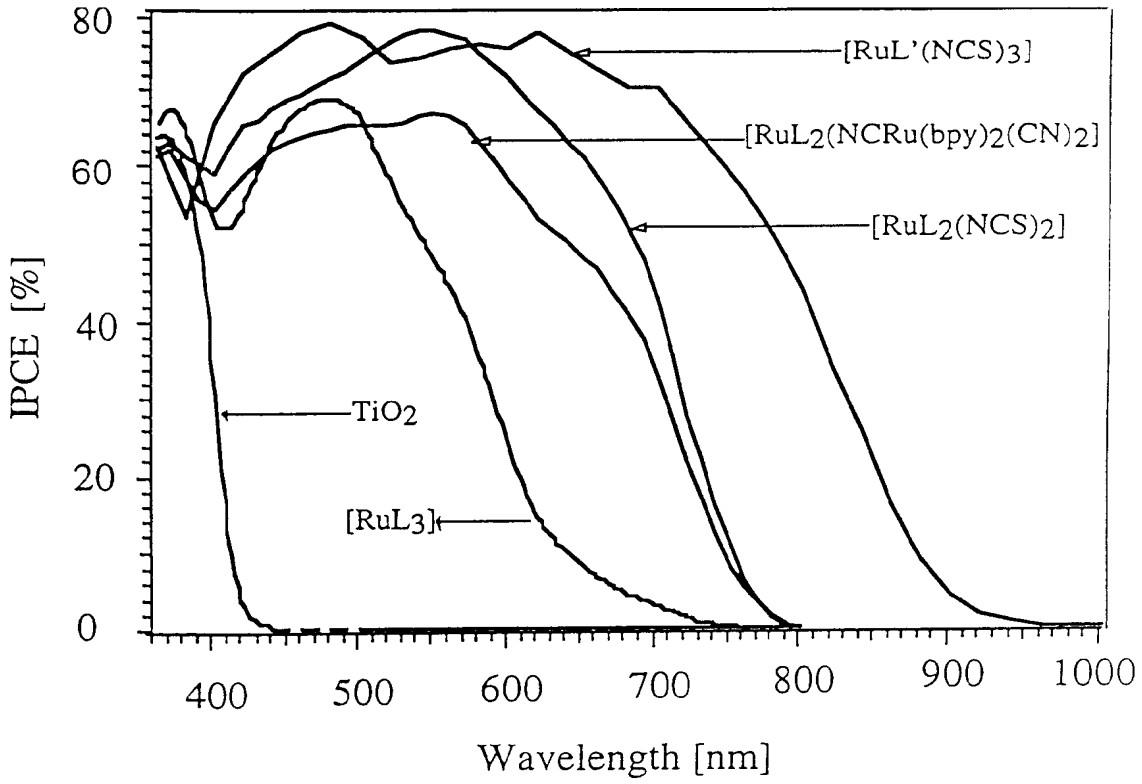


Fig. 1

Incident Photon to Current Conversion Efficiencies Obtained with Various Sensitizers



L' = 4,4',4''-tricarboxy-2,2', 6',2''-terpyridine

L = 4,4'-dicarboxy-2,2'-bipyridine

Fig. 2

The Z scheme of biphotonic water photolysis

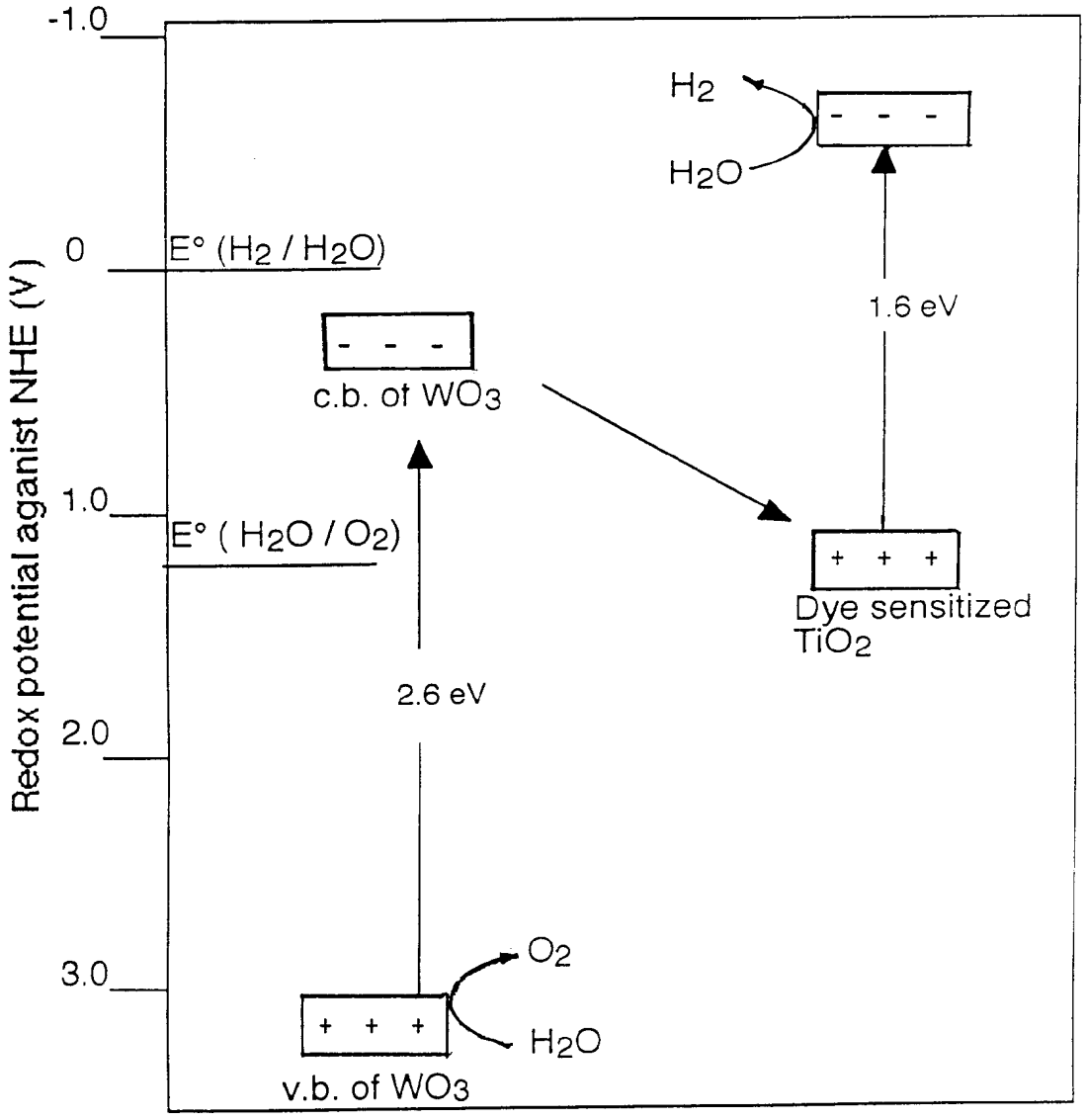


Fig. 3

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/EP 00/06350

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C25B1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BORMAN S: "HYDROGEN FROM WATER AND LIGHT" CHEMICAL AND ENGINEERING NEWS,US,AMERICAN CHEMICAL SOCIETY. COLUMBUS, vol. 76, no. 16, page 11-12 XP000740074 ISSN: 0009-2347 see whole document ---	1
A	US 3 925 212 A (DIMITER I. TCHERNEV) 9 December 1975 (1975-12-09) column 2, line 33 - line 50 column 4, line 36 -column 5, line 53 figure 3 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 November 2000	21/11/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Groseiller, P

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Interna al Application No
PCT/EP 00/06350

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB; GRATZEL M: "Photoelectrochemical solar energy conversion by dye sensitization" Database accession no. 5850979 XP002125396 abstract & FUTURE GENERATION PHOTOVOLTAIC TECHNOLOGIES. FIRST NREL CONFERENCE, DENVER, CO, USA, 24-26 MARCH 1997, no. 404, pages 119-127, AIP Conference Proceedings, 1997, AIP, USA ISSN: 0094-243X	1
A	US 4 466 869 A (WILLIAM AYERS) 21 August 1984 (1984-08-21) column 8, line 24 - line 37	1

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/EP 00/06350

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3925212 A	09-12-1975	NONE	
US 4466869 A	21-08-1984	NONE	